



# Solubility of Plutonium Compounds and Their Behavior in Soils<sup>1</sup>

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## ABSTRACT

The solubilities of  $^{239}\text{PuO}_2$  (c) (crystalline) and  $^{239}\text{Pu}(\text{OH})_4$  (am) (amorphous) under natural environmental conditions were determined. These data were then used to predict the (i) nature of the solid phases present in contaminated soils, and (ii) total concentration of Pu that can be expected in soil solutions when these Pu solids are present.

Based upon solubility measurements, an estimated value of the log  $K^c$  (equilibrium constant at room temperature and an approximate ionic strength of 0.0045) for the dissolution of  $^{239}\text{PuO}_2$ (c) [ $\text{PuO}_2\text{(c)} \rightleftharpoons \text{PuO}_2^+ + e^-$ ] was found to be -14.8. The estimated value of the log  $K^c$  for the dissolution of  $^{239}\text{Pu}(\text{OH})_4$ (am) [ $\text{Pu}(\text{OH})_4\text{(am)} \rightleftharpoons \text{PuO}_2^+ + 2 \text{H}_2\text{O} + e^-$ ] was found to be -12.8.

Comparison of Pu concentration in equilibrium solutions of contaminated Hanford soils with the  $\text{PuO}_2$ (c) and  $\text{Pu}(\text{OH})_4$ (am) solubility lines suggested that  $\text{Pu}(\text{OH})_4$ (am) was absent from all the samples and that two of the samples contained  $\text{PuO}_2$ (c). The presence of  $\text{PuO}_2$ (c) was also confirmed by X ray diffraction of Pu particles isolated from one of the samples.

**Additional Index Words**  $\text{PuO}_2$ (c),  $\text{Pu}(\text{OH})_4$ (am), equilibrium constant, plutonyl (V), oxidation reduction, redox potential.

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THE SOLID COMPOUNDS of Pu that may be present in soils have a specific solubility at equilibrium in a given weathering environment and could control the final concentration of Pu in the soil solution. The final concentration could, in turn, largely control the distribution of Pu in the environment. Therefore, knowledge of Pu compounds present in the soil and their solubility are necessary in order to predict the behavior or fate of Pu in soil.

Reliable data on the solubility of crystalline Pu oxide [ $\text{PuO}_2$ (c)] and amorphous Pu hydroxide [ $\text{Pu}(\text{OH})_4$ (am)], the compounds most likely to form in soils at environmental pH and redox potentials, are lacking (13). Based upon thermodynamic data reported in the literature, an uncertainty of at least five orders of magnitude in the solubility of these compounds is expected (14). An extensive review (2, 3) of the actinides indicate that numerous workers have studied Pu concentrations and distribution with depth in soils around nuclear installations. However, with the exception of Price and Ames (12), none have made any attempt to identify the solid phases of Pu present in soils. Price and Ames (12) isolated pluto-

onium particles from contaminated soils and analyzed them with electron microprobe and X-ray diffraction. They were able to isolate and identify discrete particles of Pu as  $\text{PuO}_2$ (c), but were not able to identify the nature of other Pu compounds associated with soil silicates. The results of Price and Ames (12) are consistent with the theoretical calculations of Rai and Serne (13) who predicted that the  $\text{PuO}_2$ (c) would be comparatively stable in the pH and redox potential ranges found in terrestrial environments.

Clearly more information is needed regarding the solubility of various Pu compounds and the nature of the solid compounds that may be present in the soils. The objectives of this study were to (i) determine Pu concentrations in equilibrium with  $\text{PuO}_2$ (c) and  $\text{Pu}(\text{OH})_4$ (am) under environmental conditions, (ii) identify Pu compounds in contaminated soils, and (iii) provide guidelines for selecting concentrations of Pu for adsorption experiments to assure that Pu precipitation would be negligible or absent.

## METHODS AND MATERIALS

The  $^{239}\text{Pu}(\text{IV})$  hydroxide used in this study was prepared by rapid neutralization of a pure  $^{239}\text{Pu}(\text{IV})$  nitrate solution (8M  $\text{HNO}_3$ ) with NaOH (6). The precipitate was washed with distilled water. The  $\text{Pu}(\text{IV})$  hydroxide thus prepared is represented in this study as  $\text{Pu}(\text{OH})_4$ (am). As expected the X ray diffraction pattern of  $\text{Pu}(\text{OH})_4$ (am) indicated it to be an amorphous compound (Table 2). The crystalline  $^{239}\text{PuO}_2$ (c) (99.1% enriched in  $^{239}\text{Pu}$ ) microspheres were obtained from Oak Ridge National Laboratory, Oak Ridge, Tennessee. A nearly perfect match of the sample d spacings with the values reported in American Society for Testing and Materials (4) indicated that the  $\text{PuO}_2$ (c) sample used for this study was indeed crystalline (Table 1). In order to determine solubility approximately 8 mg of these  $^{239}\text{Pu}$  solids were suspended in 20 ml of 0.0015M  $\text{CaCl}_2$  solution. The samples were adjusted to different pH values with HCl or NaOH. The suspensions were equilibrated with air and shaken for various lengths of time. The pH of the suspensions was periodically readjusted (approximately every fifth day) for the first 3 weeks of the experiment. The pH was measured using a glass electrode. The redox potential ( $E_m$ ) was measured with a platinum electrode (vs standard calomel electrode corrected to standard hydrogen electrode).

In order to determine the nature of the plutonium compounds present in contaminated soils, three contaminated soil samples (Z9 4 5A, Z9 4 11A, Z12 1D) from two Hanford waste disposal cribs (Z9 and Z12) were used. The samples were washed once with distilled water to remove soluble salts and then equilibrated with 0.0015M  $\text{CaCl}_2$  solution in duplicate. Equilibrations were also carried out with soil only and soil plus 5 mg of  $\text{PuO}_2$ (c). As in the case of Pu compounds the suspensions were equilibrated with air and shaken for various lengths of time.

At various times the suspensions containing Pu compounds and contaminated soils were centrifuged at 6000g for 40 min and a small aliquot of the supernate was withdrawn for Pu analyses. A preliminary analysis of these solutions indicated a wide variation (as high as 30 fold in some cases) in Pu concentrations of duplicate aliquots withdrawn from a sample. This variation was later found to be due to the inability of centrifugation to completely separate the solid particles from the solution. Filtration through (0.1 and/or 0.015  $\mu\text{m}$ ) Nuclepore® filters gave consistent analyses of duplicate aliquots and thus presumably removed the fine solid particles. The Pu activity in solutions was determined by alpha counting in a 2 $\pi$  geometry.

The crystallinity of the Pu samples was determined from X ray diffraction patterns obtained by using Cu K $\alpha$ .

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Table 1—X-ray diffraction data for Pu samples

Standard PuO <sub>2</sub> (c)	d (Å) from different Pu samples†			
	Pu used in study			
	PuO <sub>2</sub> (c)	Pu(OH) <sub>4</sub> (am)	Filtered Pu	Soil Pu
3 08	3 118	A	3 13	3 13
2 67	2 696	A	2 71	
1 894	1 909	A	1 919	1 888
1 617	1 627	A	1 631	1 623
1 548	1 559	A		1 552
1 234	1 239	A		1 235
1 203	1 208	A		1 204
1 199	1 103	A		1 098

† Standard PuO<sub>2</sub>(c) data ASTM (1966), A = amorphous, filtered Pu = Pu retained by a 0.1  $\mu$ m membrane used to filter PuO<sub>2</sub>(c) suspension no 20 equilibrated for 90 days (Table 1), soil Pu = Pu separated from contaminated soil Z9-4 11A (1)

## RESULTS AND DISCUSSION

### Solubility of Pu Compounds

The concentration of Pu in unfiltered and filtered solutions after contact with <sup>239</sup>PuO<sub>2</sub>(c) and <sup>239</sup>Pu(OH)<sub>4</sub>(am) for 90 days is given in Table 2. The samples passed through 0.1 and 0.015- $\mu$ m filters do not differ significantly from each other, indicating that discrete Pu particles >0.015  $\mu$ m and <0.1  $\mu$ m are absent from solutions. The Pu concentrations in unfiltered samples were generally close to those in the filtered solutions except in a few relatively high pH samples where the concentration in unfiltered solutions was up to three orders of magnitude higher than in the filtered solutions. Discrete particles of Pu were found when several filters employed in filtration were examined with a scanning electron microscope and an electron microprobe. X-ray diffraction patterns of the Pu retained on a 0.1  $\mu$ m membrane (Table 1) used to filter a PuO<sub>2</sub>(c) sample indicated it to be a crystalline PuO<sub>2</sub>(c). Thus, the difference in Pu concentration between the unfiltered and filtered solutions can be attributed to the incomplete separation of Pu particles from the unfiltered solutions. Therefore, all subsequent samples were filtered before analysis. At the end of the 90 day equilibration, the X-ray diffraction patterns showed that the PuO<sub>2</sub>(c) samples were crystalline and Pu(OH)<sub>4</sub>(am) samples were amorphous, as was the case at the beginning of the experiment. Thermodynamic prediction (13) and literature data (10) indicate that with time Pu(OH)<sub>4</sub>(am) will crystallize and change to PuO<sub>2</sub>(c). However, the equilibration period employed in this study apparently was not long enough for this change to occur to any measurable extent.

Plutonium concentrations in solution in contact with PuO<sub>2</sub>(c) and Pu(OH)<sub>4</sub>(am) for 90, 130, and approximately 250 days are plotted against pH in Fig 1 and 2. Values for 90, 130, and 250 days are similar, suggesting that equilibrium had been reached after 90 days. The pH of the solutions was observed to continuously decrease with time (Fig 1 and 2) presumably due to radiolysis of water caused by alpha decay. With this decrease in pH the concentration of Pu has increased proportionally again suggesting that the Pu concentrations have reached equilibrium values at all of the measured pH values. As expected (13), Pu(OH)<sub>4</sub>(am) maintains a higher Pu concentration in solution at environmental pH values than does

Table 2—Concentration of Pu in 0.0015M CaCl<sub>2</sub> solution after contact with <sup>239</sup>PuO<sub>2</sub>(c) and <sup>239</sup>Pu(OH)<sub>4</sub>(am) for approximately 90 days

Sample no	pH	Log Pu (mol/liter) in solution†		
		Unfiltered	Filtered through	
			0.1 $\mu$ m	0.015 $\mu$ m
Solutions contacting PuO <sub>2</sub> (c)‡				
13	3.80	-6.14	-6.17	-6.12
14	3.80	-6.09	-6.08	-6.05
15	4.30	-6.42	-6.60	-6.57
16	4.30	-6.43	-6.43	-6.44
18	5.40	-5.69	-7.28	-7.29
17	5.45	-6.15	-7.46	-7.47
19	7.30	-6.33	-8.70	-8.55
20	7.30	-5.62	-8.71	-8.78
Solutions contacting Pu(OH) <sub>4</sub> (am)‡				
21	3.95	-4.40	-4.44	-4.46
22	4.00	-4.54	-4.54	-4.52
5	4.00	-3.90	-4.31	ND
6	4.00	-3.39	-4.22	ND
24	5.00	-5.26	-5.25	-5.25
23	5.05	-5.43	-5.44	-5.47
8	5.25	-4.99	-5.17	ND
7	5.30	-5.19	-5.31	ND
26	6.60	-6.51	-6.77	-6.79
25	6.70	-6.56	-6.83	-6.98
10	6.80	-5.18	-6.63	ND
9	6.83	-5.71	-6.73	ND
27	7.50	-7.43	-7.54	-7.58
28	7.70	-7.19	-7.77	-7.79
12	7.85	-5.21	-7.11	ND

† All solutions were centrifuged at 6 000g for 40 min, ND = not determined, the average values of three subsamples counted from each sample are given and the error (one standard deviation) in all the samples was <  $\pm 0.06$  except in unfiltered PuO<sub>2</sub>(c) samples 19 and 20 and Pu(OH)<sub>4</sub>(am) samples 7 and 9 where the error varied from  $\pm 0.13$  to  $\pm 0.18$ .

‡ Approximately 8 mg of crystalline PuO<sub>2</sub> or amorphous Pu(OH)<sub>4</sub> were shaken with 20 ml of 0.0015M CaCl<sub>2</sub>.

PuO<sub>2</sub>(c). The solubilities of both PuO<sub>2</sub>(c) and Pu(OH)<sub>4</sub>(am) decrease with increasing pH. Linear relationships exist between the pH and total Pu concentration in solution in equilibrium with the different Pu compounds. These relationships for PuO<sub>2</sub>(c) (Eq [1]) and for Pu(OH)<sub>4</sub>(am) (Eq [2]) are

$$\log (\text{Pu}_{\text{total}}) = (-3.90 \pm 0.10) - (0.64 \pm 0.02) \text{ pH} \quad [1]$$

$$\log (\text{Pu}_{\text{total}}) = (-1.19 \pm 0.08) - (0.80 \pm 0.01) \text{ pH} \quad [2]$$

where  $\text{Pu}_{\text{total}}$  is in mol/liter. The measured redox potentials ( $E_m$  in V) and pH of PuO<sub>2</sub>(c) and Pu(OH)<sub>4</sub>(am) suspensions (Fig 3) also exhibited a linear correlation as shown in Eq [3].

$$E_m = (0.727 \pm 0.011) - (0.0545 \pm 0.0008) \text{ pH} \quad [3]$$

Rai et al (15) have shown that the solutions in equilibrium with Pu(OH)<sub>4</sub>(am) contain mainly Pu(V). Their results also strongly suggest the presence of Pu(V) in solutions contacting PuO<sub>2</sub>(c). Pu(V) would be expected to be present predominantly as PuO<sub>2</sub><sup>+</sup> in these solutions because (i) the relative tendency of Pu ions to form complexes is Pu(IV) > Pu(III) > Pu(VI) > Pu(V) (7), (ii) the only anion present in these solutions in significant amounts is Cl<sup>-</sup>, which does not form significant complexes with PuO<sub>2</sub><sup>+</sup> (13), and (iii) the species PuO<sub>2</sub><sup>+</sup> remains without further hydrolysis between pH zero and pH of approximately 8 (5, 13). Therefore, the  $\text{Pu}_{\text{total}}$  in Eq [1] and [2] can be replaced with PuO<sub>2</sub><sup>+</sup>. Thus Eq [1] and [2] can now

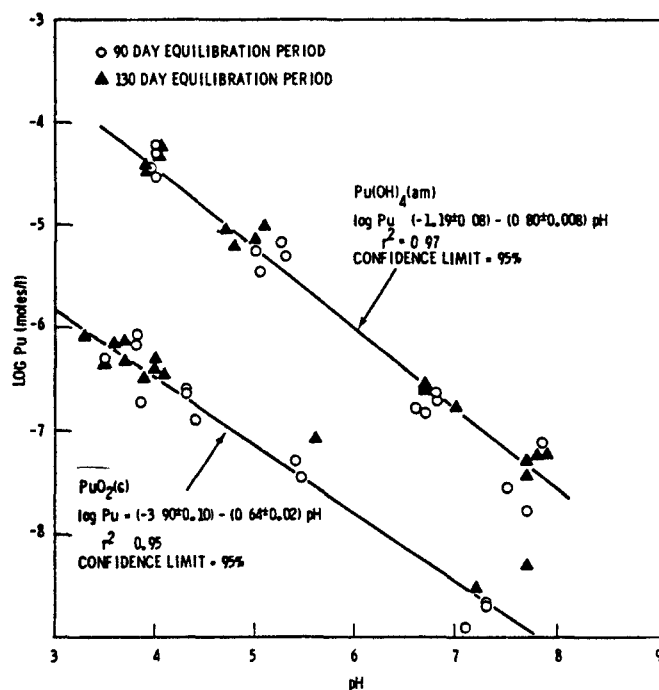


Fig 1—Concentration of Pu in filtered (0.1  $\mu$ m) solutions after approximately 90 and 130 days of contact of 0.0015M  $\text{CaCl}_2$  with  $^{239}\text{PuO}_2(\text{c})$  and  $^{239}\text{Pu}(\text{OH})_4(\text{am})$

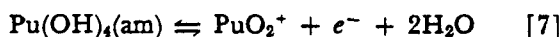
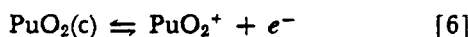
be written as Eq [4] and [5], respectively

$$\log (\text{PuO}_2^+) = (-3.90 \pm 0.10) - (0.64 \pm 0.02) \text{ pH} \quad [4]$$

$$\log (\text{PuO}_2^+) = (-1.19 \pm 0.08) - (0.80 \pm 0.01) \text{ pH} \quad [5]$$

#### Estimation of Equilibrium Constants

The solubility of  $\text{PuO}_2(\text{c})$  and  $\text{Pu}(\text{OH})_4(\text{am})$  is written (Eq [6] and [7]) in terms of  $\text{PuO}_2^+$ , because the  $\text{PuO}_2^+$  is shown to be the solution species in equilibrium with these compounds (15)



The products and reactants in Eq [6] and [7] are related to the equilibrium constant ( $K^0$ ) as follows

$$\log K^0 = \log [\text{PuO}_2^+] - pe \quad [8]$$

where [ ] around  $\text{PuO}_2^+$  denotes activity and the  $pe$  refers to the negative log of the electron activity. The  $pe$  is related to the electrochemical potential ( $E_h$  in V) (18) by

$$pe = 16.9 E_h \quad [9]$$

For reasons discussed later in this paper, it is inferred that the  $E_m$  values are similar to  $E_h$  values. Therefore,  $pe$  can be calculated from Eq [9] for its use in estimating the equilibrium constants. Substituting the value of  $E_m$  (Eq [3]) into Eq [9]

$$pe = (16.9) [(0.727 + 0.011) - (0.0545 \pm 0.0008) \text{ pH}] \quad [10]$$

Substituting Eq [4] or [5] and Eq [10] into Eq [8] and simplifying, the log of the equilibrium concentration constant ( $\log K^c$ ) at room temperature and

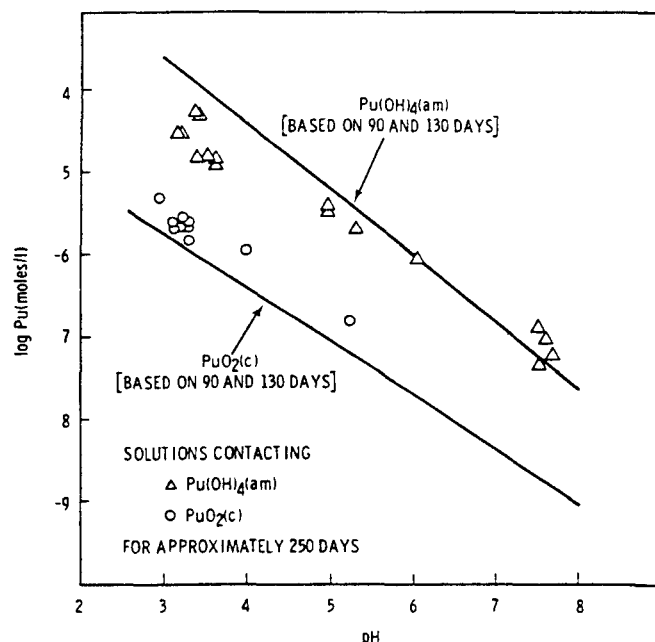


Fig 2—Concentration of Pu in filtered (0.1  $\mu$ m) solutions after approximately 250 days of contact of 0.0015M  $\text{CaCl}_2$  with  $^{239}\text{PuO}_2(\text{c})$  and  $^{239}\text{Pu}(\text{OH})_4(\text{am})$

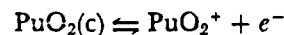
low ionic strength ( $\approx 0.0045$ ) for the dissolution of  $\text{PuO}_2(\text{c})$  according to Eq [6] can be written as

$$\log K^c = (-16.19 \pm 0.21) + (0.28 \pm 0.02) \text{ pH} \quad [11]$$

and the  $\log K^c$  for the dissolution of  $\text{Pu}(\text{OH})_4(\text{am})$  according to Eq [7] can be written as

$$\log K^c = (-13.48 \pm 0.20) + (0.12 \pm 0.02) \text{ pH} \quad [12]$$

Equations [11] and [12] hold for a pH range of approximately 4 to 8 (Fig 1). The errors quoted in Eq [11] and [12] were calculated using a propagation of errors method described by Mandel (9).  $\log K^c$ , at fixed ionic strength and temperature, by definition is a constant. However,  $\log K^c$  in Eq [11] and [12] shows a dependence upon pH (approximately 2% deviation per pH unit). This dependence on pH is likely due to experimental errors in measuring  $\text{PuO}_2^+$ , pH, and  $E_m$ . The estimated value of  $\log K^c$  for

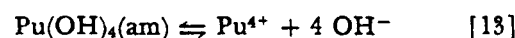


at the average pH (4.8) value of solutions contacting  $\text{PuO}_2(\text{c})$  is  $-14.8$ . The estimated value of  $\log K^c$  for



at the average value of pH (5.8) of solutions contacting  $\text{Pu}(\text{OH})_4(\text{am})$  is  $-12.8$ . It should be mentioned that the solutions are of low ionic strength ( $\approx 0.005$ ) and thus the concentration equilibrium constant ( $K^c$ ) is approximately equal to the thermodynamic equilibrium constant ( $K^0$ ).

A literature review was done in order to compare the equilibrium constants determined in this study with the reported values. A  $\log K^0$  for



based upon solubility measurements in solutions of pH  $< 3.5$  is reported by Perez Bustamante (11) to vary

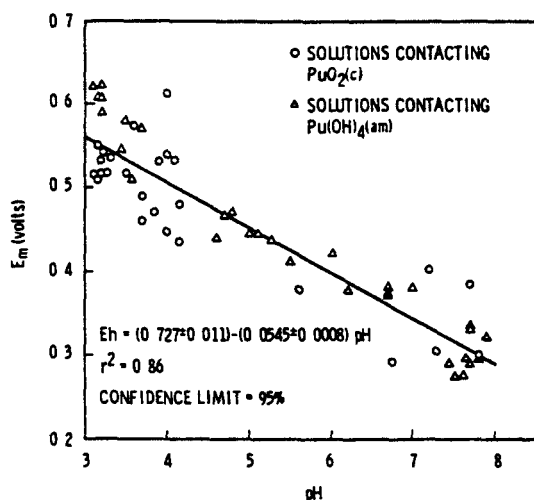


Fig 3—Relationship of measured redox potential ( $E_m$ ), with respect to standard hydrogen electrode, and pH of solutions contacting different  $^{239}\text{Pu}$  solids

from  $-47.3$  to  $-56.3$ . Baes and Mesmer (5) reported  $\log K^0$  for Eq [13] to vary from  $-52.0$  to  $-56.0$ . Smith and Martell (17) selected a value of  $-47.3$  which they believed best represents the  $\log K^0$  for this reaction. Clearly, there is wide variation and disagreement in reported values for the solubility product of  $\text{Pu}(\text{OH})_4(\text{am})$ . Based upon the results obtained in the present study, the  $\log K^0$  for the solubility product of  $\text{Pu}(\text{OH})_4(\text{am})$  (Eq [13]) can be estimated in the following manner:

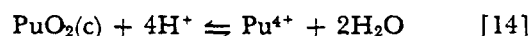
	$\log K^0$	Reference
$\text{Pu}(\text{OH})_4(\text{am}) \rightleftharpoons \text{PuO}_2^+ + 2 \text{H}_2\text{O} + e^-$	$-12.8$	Present study
$\text{PuO}_2^+ + 4 \text{H}^+ + e^- \rightleftharpoons \text{Pu}^{4+} + 2 \text{H}_2\text{O}$	$18.6$	(8)
$4 \text{H}_2\text{O} \rightleftharpoons 4 \text{H}^+ + 4 \text{OH}^-$	$-56.0$	(16)
$\text{Pu}(\text{OH})_4(\text{am}) \rightleftharpoons \text{Pu}^{4+} + 4 \text{OH}^-$	$-50.2$	[13]

Assuming the thermodynamic data used in the above equations is correct, an estimated  $\log K^0$  of  $-50.2$  for the solubility product of  $\text{Pu}(\text{OH})_4(\text{am})$  is obtained. We prefer to represent the solubility of  $\text{Pu}(\text{OH})_4(\text{am})$  as described by Eq [7] rather than Eq [13], because there is a large possibility of error in the thermodynamic data used to derive Eq [13]. Nevertheless, the estimated solubility product of  $\text{Pu}(\text{OH})_4(\text{am})$  obtained in this study is certainly within the range of values reported.

There are no data available in the literature for the measured solubility constant of  $\text{PuO}_2(\text{c})$  for comparison with this study. Baes and Mesmer (5) calculated the solubility of  $\text{PuO}_2(\text{c})$  based upon the thermodynamic data and compared it with the reported  $\log K^0$  values ( $-52$  to  $-56$ ) of the solubility product of  $\text{Pu}(\text{OH})_4(\text{am})$  and found a great difference (approximately 12 log units) between them. They report that such great differences between the precipitated hydrous oxide and the oxide are unusual and suggested that the reported values for  $\text{PuO}_2(\text{c})$  and/or  $\text{Pu}(\text{OH})_4(\text{am})$  are probably in error by several log units. The difference (2 log units) between the  $\log K^0$  of  $\text{PuO}_2(\text{c})$  and  $\text{Pu}(\text{OH})_4(\text{am})$  found in the present study is low as predicted by Baes and Mesmer (5) but is considerably smaller than their

estimated difference (8 log units) based upon the extrapolation of  $\log K^0$  vs the reciprocal of the lattice parameters of the actinide dioxides.

Making meaningful redox measurements, hence  $p_e$ , in unpoised solutions with a platinum electrode is difficult. If reliable values of the equilibrium constant and the  $\text{PuO}_2^+$  activity in solution were available, accurate values of  $p_e$  and/or redox potential could then be calculated from Eq [8]. The values of redox potential thus calculated for  $\text{PuO}_2(\text{c})$  and  $\text{Pu}(\text{OH})_4(\text{am})$  suspensions should be similar to each other, as was the case in measured redox potentials (Fig 3), because the study was conducted using the same isotope of Pu and under similar experimental conditions. Plutonyl ( $\text{PuO}_2^+$ ) concentrations measured in this study were all  $> 10 \times 10^{-9} M$ , where accurate measurements of Pu concentration can be made. Baes and Mesmer (5) estimated the  $\log K^0$  value of  $-6.5$  for the dissolution of  $\text{PuO}_2(\text{c})$  (Eq [14]):



Perez Bustamante (11) reported the  $\log K^0$  for the solubility product of  $\text{Pu}(\text{OH})_4(\text{am})$  (Eq [13]) to vary from  $-47.3$  to  $-56.3$ . Assuming these reported  $\log K^0$  values are correct, redox potentials were calculated using these  $\log K^0$  values and the measured  $\text{PuO}_2^+$  concentrations in Eq [8] and [9]. The redox potential thus calculated,  $E_c$ , for  $\text{PuO}_2(\text{c})$  reaction (Eq [8]) was approximately 0.61 V higher than the  $E_m$ . The calculated  $E_c$  for  $\text{Pu}(\text{OH})_4(\text{am})$  suspension was found to vary approximately from 0.17 V lower to 0.36 V higher than the  $E_m$ . We conclude from these data that the reported value (5) for  $\text{PuO}_2(\text{c})$  solubility is in error and that the measured  $E_m$  may truly represent the equilibrium potential of our suspensions which supports usage of our calculated  $\log K^0$  values as true equilibrium constants. The specific reasons for this conclusion are: (i) the measured  $E_m$  for  $\text{PuO}_2(\text{c})$  and  $\text{Pu}(\text{OH})_4(\text{am})$  suspensions are similar (Fig 3) as expected, whereas the  $E_c$  for  $\text{PuO}_2(\text{c})$  and  $\text{Pu}(\text{OH})_4(\text{am})$  are significantly different, (ii) the  $E_m$  for  $\text{Pu}(\text{OH})_4(\text{am})$  suspension falls within the range of  $E_c$ , (iii) the  $E_c$  of  $\text{PuO}_2(\text{c})$  suspensions fall outside the water stability region, and (iv) the  $E_c$  of  $\text{PuO}_2(\text{c})$  falls in the  $\text{PuO}_2^{2+}$  stability region, whereas the Pu species in solution were inferred to be  $\text{PuO}_2^+$  (13). The measured redox potentials (Fig 3) appear to be poised. This poising is hypothesized to be due to relatively high concentrations of Pu in the low pH region and/or radiolysis products of water caused by alpha decay. Further studies with the use of redox buffers and solid compounds of different alpha emitting isotopes have been initiated to check these hypotheses.

#### Identification of Pu Compounds from Contaminated Soils

The presence of Pu compounds in sediments implies that the concentration of Pu in solution will be governed by the solubility of the Pu compounds. Thus, it is important to determine the nature of the solid compounds that may be present in sediment. If no Pu solid compounds are present, sorption reactions alone may govern the concentration of plutonium in solutions.

Large quantities of Pu solids would not be expected

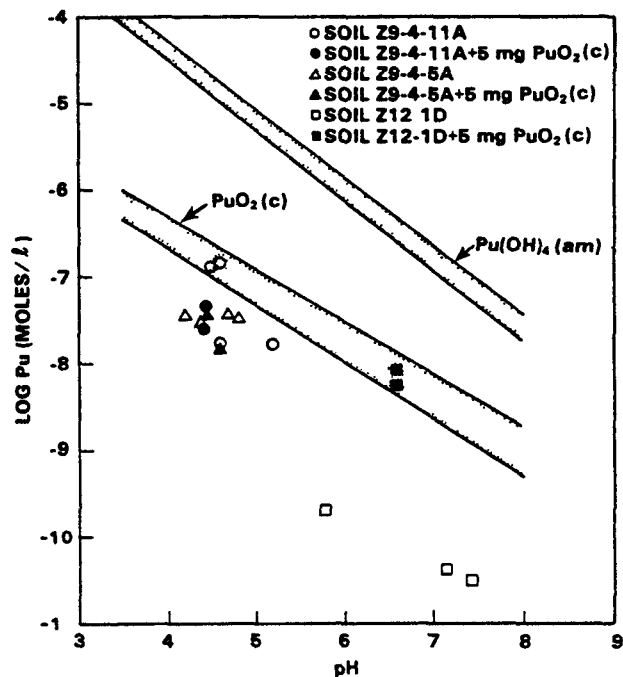


Fig 4—Concentration of Pu in filtered (0.1  $\mu$ m) solutions contacting contaminated Hanford soils with different treatments

to be present in sediments. Therefore, it would be difficult to physically isolate, for identification, the trace amounts of Pu solids that may be present in sediments. It was decided to compare the plutonium concentrations in soil solutions with the experimental solubility of the solid compounds as a means of possibly identifying the plutonium solids that may be present in the sediments.

The soil solution data are plotted in Fig 4 where experimental solubility lines for  $\text{PuO}_2(\text{c})$  and  $\text{Pu}(\text{OH})_4(\text{am})$  are also traced for reference. Soil solution points for soils Z9-4-11A and Z9-4-5A fell very near the  $\text{PuO}_2(\text{c})$  solubility line, however, the solution points for soil Z12-1D fell considerably below the  $\text{PuO}_2(\text{c})$  solubility line. When  $\text{PuO}_2(\text{c})$  was added to these suspensions the solution concentration for Z9-4-11A and Z9-4-5A did not change appreciably. The solution concentration for Z12-1D soil increased considerably and approached that of the  $\text{PuO}_2(\text{c})$  solubility line. Thus, soils Z9-4-11A and Z9-4-5A appear to contain  $\text{PuO}_2(\text{c})$  since the soil solution points fell close to the  $\text{PuO}_2(\text{c})$  solubility line and the soil solution concentration did not change appreciably with the addition of  $\text{PuO}_2(\text{c})$ . The presence of crystalline  $\text{PuO}_2(\text{c})$  in Z9-4-11A sample, inferred from the solubility data, was confirmed by X-ray diffraction analysis of Pu particles isolated from this sample (Table 1). Concentrations of Pu in solutions containing soil Z12-1D indicate that this soil does not contain  $\text{PuO}_2(\text{c})$ .

The Pu concentration in all the soil solutions studied were much lower than the  $\text{Pu}(\text{OH})_4(\text{am})$  solubility line, indicating that the soils do not contain this compound.

The results presented above help demonstrate the ability of solid compounds to control the solution concentrations. If leaching occurs from Z9-4-11A and Z9-4-5A soils and the leachate percolates into the soils containing no  $\text{PuO}_2(\text{c})$ , the concentration of Pu in

solution would be lower than the  $\text{PuO}_2(\text{c})$  solubility line and would be governed by sorption reactions. On the other hand, Pu concentrations in solutions percolating through  $\text{PuO}_2(\text{c})$  contaminated sediments would be expected to be similar to the concentrations predicted from the  $\text{PuO}_2(\text{c})$  solubility line (Fig 1). Such an event might occur in the immediate vicinity of stored wastes. It is also evident that for the determination of meaningful equilibrium distribution coefficients ( $K_d$ ), in an oxidizing environment, the Pu concentrations must be below the  $\text{Pu}(\text{OH})_4(\text{am})$  solubility line [and preferably below the  $\text{PuO}_2(\text{c})$  solubility line] (Fig 1).

Two of the soil samples studied (Z9-4-11A and Z9-4-5A) in this report had received a complex waste with significant amounts of organic ligands with strong potential for forming soluble Pu complexes. However, the observed Pu concentrations are not significantly different than the concentrations present in a dilute  $\text{PuO}_2(\text{c})$  suspension devoid of organic ligands. It is inferred that the organic ligands originally disposed into these soils have degraded over the period when the wastes were first disposed (approximately 20 years). This inference is supported by the results of Cleveland (J. M. Cleveland, Chief, Transuranium Research Project, USGS, Denver, Colorado, Personal Communication, September 1977) who did not find detectable amounts of organics in Rocky Flats soil that had been contaminated by lathe cooling oil.

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## A Comparative Electron Spin Resonance Study of $\text{VO}^{2+}$ Complexation in Synthetic Molecules and Soil Organics<sup>1</sup>

M B MCBRIDE<sup>2</sup>

### ABSTRACT

The vanadyl ion,  $\text{VO}^{2+}$ , has been used as an ESR (electron spin resonance) probe of adsorption sites in pure organic complexing agents and natural peat to obtain information on the nature of the metal-organic bond in soils. Oxygen ligands of soil organics displace on the average about two ligand  $\text{H}_2\text{O}$  molecules from  $\text{VO}(\text{H}_2\text{O})_6^{2+}$  in forming an inner-sphere complex with the metal. The bonding mechanism of natural organics is very similar to that of polycarboxylic acids such as uronic acid. Unlike soluble low molecular weight carboxylic acids, the solid polycarboxylates are not able to bond to all four equatorial ligand positions of  $\text{VO}(\text{H}_2\text{O})_6^{2+}$ . Evidence is presented that Fe and Al in the soil organics occupy complexation sites and partially block  $\text{VO}^{2+}$ -carboxylate bond formation. The heterogeneous nature of natural organic complexing sites is demonstrated by the broadened nature of  $\text{VO}^{2+}$  ESR spectra when the metal is adsorbed on soil organics in comparison with pure polycarboxylic acids.

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METAL BONDING on soil organics has been investigated in the past by numerous techniques, although most have not been able to indicate directly the nature of the bonding site. Nevertheless, it has generally been assumed that carboxylic and phenolic groups are largely involved, and that chelation of metals occurs. More recent studies using electron spin resonance (ESR) have provided a clearer picture of the mechanism of metal bonding. For example,  $\text{Mn}^{2+}$  has been found to retain a hydration shell when adsorbed on soil organics (Gamble et al, 1977, McBride, 1978), while  $\text{VO}^{2+}$  and  $\text{Cu}^{2+}$  bond directly to oxygens of functional groups (Lakatos et al, 1977, Goodman and Cheshire, 1975, Bresnahan et al, 1978, McBride, 1978). The ESR spectrum of  $\text{VO}^{2+}$  is particularly useful in providing information on the stereochemistry, ligand type, and degree of covalency of the metal-organic complex. For this reason, the present study was undertaken to compare the spectral features of  $\text{VO}^{2+}$  bound into various synthetic and natural organic compounds. Such a comparison could, in prin-

ciple, reveal the nature of complexing sites in soil organics.

### MATERIALS AND METHODS

Soluble  $\text{VO}^{2+}$  organic species were investigated by adding 25 ml of 0.01M  $\text{VOSO}_4$  to 25 ml of 0.01M solutions of  $\text{Na}^+$ -salicylate, -phthalate and -benzoate initially adjusted to a pH near 2 with 0.1N HCl. Titration of the solution with 0.1N NaOH to higher pH was then conducted until oxidation of the  $\text{VO}^{2+}$  was observed. During the titration small samples of solution at measured pH values were collected in capillary tubes and analyzed by ESR. A similar ESR titration was done with  $\text{Na}^+$ -carboxymethylcellulose (250 mg) with 5 ml of 0.01M  $\text{VOSO}_4$ , added since the material was soluble in water.

A series of polymeric organic acids was chosen for comparison with natural organics. These included sulfonate resin (Rexyn RG 50) polymethacrylate resin (Amberlite IRC 50) pectic acid, carboxymethylcellulose and polygalacturonic acid. A 250 mg sample of each material was mixed with 5 ml of aqueous 0.01M  $\text{VOSO}_4$ , and the ESR spectra of the adsorbed  $\text{VO}^{2+}$  were obtained on a Varian E 104 (X band) spectrometer with the samples moist and unwashed. A purified humic acid was also investigated by ESR after reacting 2 ml of 0.01M  $\text{VOSO}_4$  with 100 mg of the organic.

A peat sample obtained from a New York muck soil was doped with  $\text{VO}^{2+}$  by adding 5 ml of 0.01M  $\text{VOSO}_4$  to 0.50 g and washing once to remove excess salt. The solid material in the moist state was then analyzed by ESR. The procedure was repeated for peat samples that had been pretreated with 0.3M  $\text{Na}^+$ -citrate, 0.3M  $\text{Na}^+$ -citrate and  $\text{Na}$ -dithionite and 0.5M  $\text{AlCl}_3$ . After 1 hour of shaking with these reagents excess reagents were removed by three water washings. The  $\text{VO}^{2+}$  was then added as in the peat sample that was not pretreated. The treatments involving citrate solubilized a significant fraction of the peat which was then discarded in the washing procedure.

To test the effect of pH on the bonding of  $\text{VO}^{2+}$  by a natural and a model carboxylic acid solid 0.500 g of peat and polygalacturonic acid were placed in separate beakers. 10 ml of 0.01M  $\text{VOSO}_4$  was added to each and the pH was adjusted to 2 with 0.1N HCl. The two materials were then titrated to a higher pH and small samples of the suspensions were removed for analysis by ESR in order to obtain spectra over a wide range of pH. The polygalacturonic acid became more soluble at higher pH and appeared to form a solution by the time the pH had been adjusted to 7.

### RESULTS

The ESR spectrum of aqueous  $\text{VO}^{2+}$  at room temperature consists of eight resonances arising from the interaction between the single unpaired d electron of vanadium and the nuclear spin ( $I = 7/2$ ). The  $\text{VO}(\text{H}_2\text{O})_6^{2+}$  ion tumbles rapidly enough in solution to average anisotropies of the hyperfine splitting, and a single splitting value,  $a_0$ , can be determined by dividing the separation of the outer hyperfine lines by seven (Fig 1a). This value is 115.6-116.0 G for aque-

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